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"Formation and Deactivation Processes in
Electronic Transitions, Chemically Pumped Lasers"

by

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The present research program was concerned with measurement of the rates of formation of excess populations of electronically excited small molecules, particularly in chemiluminescent metal + oxidant reactions, and characterization of the deactivation processes which tend to relax these excited states. One of the motivations for these investigations was the possibility of finding a suitable candidate for a chemically - pumped, electronic transition (i.e., visible - wavelength) laser system. Although such a system was not developed in the course of this work, a great deal of information on the pertinent reaction and relaxation rates was obtained. Initially, this program was under the joint direction of Profs. J.L. Gole and J.I. Steinfeld at M.I.T.; Prof. Gole moved his part of the research to the Georgia Institute of Technology during the final year of the grant. For convenience, we summarize here the principal findings arising from the overall research program; more details can be found in the cited reference(s) from the publications list which follows.

1. Aluminum - Ozone Reaction. The reaction of aluminum with ozone produces the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ emission spectrum of AlO. Coupling between the $B^2\Sigma^+$ and $A^2\Pi$ levels of AlO is attributed to perturbations (Lindsay and Gole, 1977).

2. Lanthanum - Oxidant Reactions. Reaction of lanthanum with oxidants (O_2 , NO_2 , N_2O , O_3) results in chemiluminescent emission from the $A^2\Pi$, $B^2\Sigma^+$, $C^2\Pi$, and in the latter three instances the $D^2\Sigma^+$ states of LaO. The dissociation energy of LaO and a potential function for its $D^2\Sigma^+$ state have been deduced from the data. The electronic state distribution

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in the La + O₂ reaction has been shown by Levine and Ben-Shaul to follow a simple zero-surprisal form (Gole and Chalek, 1976).

3. Reactions of Silanes and Boranes with Oxidants. The reactive systems B₂H₆ + O₃, F₂; B₅H₉ + O₃, F₂; and Si₂H₆ + O₃, F₂ have been studied. The B₂H₆ + O₃ and B₅H₉ + O₃ systems yield primarily BO₂* with some BO*. The B₂H₆ + F₂ and B₅H₉ + F₂ systems yield HBF* and BH*. The Si₂H₆ + O₃ system is believed to yield HSiO. The reaction of disilane (Si₂H₆) with F₂ is characterized by strong emission from the A² Σ^+ - X² Π transition of SiF, the A(²B₁) - X(²A₁) transition of SiF₃, and the A² Δ - X² Π transition of SiH. By contrast, the principal emission from monosilane - chlorine or disilane - chlorine reactions is the ¹A" - ¹A' transition of HSiCl. An attempt was made to run the B₅H₉ + F₂ reaction in a laser cavity, but stimulated emission was not observed (Conner *et al.*, 1977).

4. Scandium and Yttrium Oxidation Reactions. The reactions of Sc and Y with O₂ are characterized by emission from the A² Π and the previously unobserved A'² Δ states of ScO and YO. The reactions of Sc and Y with NO₂, N₂O and O₃ result in emission from the A² Π and B² Σ^+ states of ScO and YO. Dissociation energies of ScO and YO [D₀⁰(YO) \geq 7.49 eV] have been deduced from the data (Chalek and Gole, 1977).

5. Titanium-Oxidant Reactions. The reaction of Ti with O₂, NO₂, and N₂O results in chemiluminescent emission from the B³ Π and C³ Δ states. From analysis of the temperature dependence, we conclude that Ti(⁵F) excited atoms are the most likely precursors of the C³ Δ state (Dubois and Gole, 1977).

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6. Chemiluminescent Reactions of the Group IIIB Metals. The reactions of scandium, yttrium, and lanthanum with F_2 , Cl_2 , Br_2 , SF_6 , ClF , and IBr have been studied under "single collision" conditions using a beam-gas arrangement. The observed chemiluminescent spectra are primarily attributed to emission from the metal monohalides. Dihalide emission is also observed in the $Sc-Br$ and $Sc-Cl$ systems. We find extremely selective production of monohalide excited electronic states in both the scandium and yttrium reactions. The lanthanum reactions are characterized by relatively moderate selective excitation of monohalide excited states. The selective feature dominating the scandium and yttrium monohalide spectra has not been observed by previous researchers. On the basis of molecular orbital theory, energy conservation, and known spectra for scandium and yttrium fluoride, the selective emission feature is assigned to a $^3\Sigma^+ - ^1\Sigma^+$ or $^3\Sigma^+ - ^3\Delta$ band system. We have determined the molecularity with respect to oxidant for all reactions studied, monitoring chemiluminescent intensity versus oxidant pressure. All reactions producing metal monofluoride are found to be first order with respect to oxidant while reactions producing the monochloride or monobromide are found to be "faster than first order." This behavior is explained in terms of the kinetics of metastable excited states. The production of $ScCl_2$ and $ScBr_2$ also occurs via a "faster than first order" process. Based upon mechanistic considerations entailed in the kinetics of metastable excited states, the radiative lifetimes of the selectively populated excited states of $ScCl$, $ScBr$, and YCl are estimated to be on the order of 2×10^{-3} seconds. Analysis of the temperature dependence for six representative reactions indicates that selective

excited state formation of the metal monohalides proceeds by a direct mechanism with negligible activation energy. From the short wavelength limits of the chemiluminescent spectra, lower bounds to the dissociation energies of the monohalides have been determined. For some of the chemiluminescent reactions studied, we have found evidence for "super-relaxation" on collision.

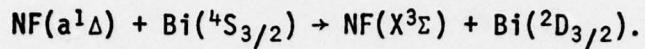
In the reactions of Group IIIB metals with F_2 and NO_2 , cross sections for excited-state metal monohalide formation considerably exceed those for monoxide formation. The experimentally determined cross sections are compared with total reactive cross sections, calculated on the basis of mechanistic models used to describe the oxidation reactions of Group IIIB atoms. Based upon this comparison, the ratio of excited state to ground state formation (quantum yield) is determined to be not less than 0.1 for the monohalides (Chalek *et al.*, 1976; Gole *et al.*, 1977; Preuss and Gole, 1977).

7. Optical Model for Surface Crossing. Several approaches were investigated to the problem of calculating the rates of collision-induced relaxation between molecular electronic states. Following a classical trajectory("surface-hopping") study of $I_2^* B^3\Pi_{ou}^+ \rightarrow ^3\Pi_g$ (dissociative), the same system was analyzed using an equivalent optical-potential model which yielded a great saving in computation time. This model was also applied to the $N_2^* B^3\Pi \rightarrow (A^3\Sigma, W^3\Delta)$ system, but difficulties were encountered with $\Omega \neq 0$ systems, such as $CN A^2\Pi$. The Landau-Zener calculation of the probabilities employed in the optical model was also compared with more recent semiclassical scattering theories (Garetz *et al.*, 1975, 1976; Bendazzoli *et al.*, 1977).

8. Information-Theoretic Analysis of Deactivation Rates. The Information-Theoretic treatment of nonequilibrium processes, due to Levine and Bernstein, has proven to be remarkably useful for characterizing relaxation processes, and several aspects of applying these methods were investigated in this program. A set of state-to-state rates for V-V relaxation in HF was calculated by the "Surprisal Synthesis" method (work performed at Air Force Weapons Laboratory, Kirtland AFB), and the nonlinear master equation governing V-V equilibration in HF was solved using exponential-gap rate constants, in collaboration with Professor R.D. Levine (Steinfeld, 1978; Tabor et al., in press).

9. Spectroscopy and Deactivation of CN A²Π. Laser action has been observed from the CN A state produced by photodissociation or electric-discharge pumping, and this system has also been suggested as a promising candidate for a chemically-pumped laser system. Since little is known about the quenching of this state, several investigations were undertaken. Some 39 bands of the "Berkeley" atlas of the CN A²Π - X²Σ transition, along with 16 bands measured at high resolution by R. Bacis of the University of Lyon, were reanalyzed with a least-squares technique, allowing for all (A²Π ~ X²Σ) and (A²Π ~ B²Σ) perturbations. This provided mixing coefficients for the perturbed levels in the A state. The analysis is currently being completed in collaboration with Dr. J.A. Coxon, Dalhousie University, Halifax, Nova Scotia. Attempts to carry out monochromatically excited fluorescence experiments on selected levels of the CN A state were, however, inconclusive (Kotlar et al., to be published).

10. Near-Resonant Electronic Energy Transfer. In collaboration with Dr. D. Sutton of the Aerospace Corporation, a measurement was carried out of the rate constant for the nearly resonant ($\Delta E = 16 \text{ cm}^{-1}$) energy transfer process,



The measured value, $1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ($\sigma \approx 200 \text{ \AA}$), is one of the largest that has been observed for such a process. Since both optical transitions are highly forbidden, a simple dipole interaction model cannot account for this observation. A technically important example of such a process is the chemically pumped $\text{O}_2^*(\text{^1}\Delta) - \text{I}$ atom transfer laser recently developed at AFWL (Capelle *et al.*, *in press*).

11. Multiphoton CO₂ Laser Vibrational Heating of Metastable Electronic States. Biacetyl molecules, prepared in the triplet metastable state by intersystem crossing from the $^1\text{A}_\text{u}$ electronic state which in turn is excited by irradiation with the 457.9 nm line of a cw Ar⁺ laser, are pumped by an intense CO₂ laser pulse which excites the system vibrationally. Changes in the luminescence characteristics of the electronically excited molecules induced by the infrared pulse are studied in various visible spectral regions. In the region characteristic of the biacetyl phosphorescence, a fast decay of the phosphorescence is observed. A burst of delayed fluorescence is observed in the fluorescence region of the biacetyl; this signal is characterized by a very fast rise time. Both fluorescence and phosphorescence signal exhibit the same decay time.

Attenuation of the CO₂ laser beam results in an increase of the decay time and in a decrease of the amplitudes of the fluorescence signal.

The experimental results are explained in terms of mixed singlet-triplet vibronic wave functions, characterizing the triplet vibrational manifold, with vibrational energy exceeding the $^1A_u - ^3A_u$ energy separation. A calculation of the decay times as a function of the absorbed CO₂ laser energy, which is based on a recent model for delayed fluorescence, gives good agreement with the experimental data. This is the first well-characterized example of reverse intersystem crossing resulting from multiple infrared photon excitation of vibrational modes, which are then converted into electronic excitation (Burak et al., in press; preprint enclosed with this report).

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Research was performed on the rates of formation of excess populations of electronically excited small molecules, particularly in chemiluminescent metal + oxidant reactions, and characterization of the deactivation processes which tend to relax these excited states. Results were obtained in the following areas: (1) aluminum + ozone reaction; (2) lanthanum + oxidant reactions; (3) reactions of silanes and boranes with oxidants; (4) scandium and yttrium oxidant reactions; (5) titanium + oxidant reaction; (6)		

chemiluminescent reactions of the Group IIIB metals; (7) optical model for surface crossing; (8) Information-Theoretic analysis of deactivation rates; (9) Spectroscopy and deactivation of CN(A²D); (10) near-resonant electronic energy transfer; and (11) multiphoton CO₂ laser vibrational heating of metastable electronic states.

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